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A. V. BLEININGER, Director

SOME CHEMICAL AND PHYSICAL CHANGES IN CLAYS DUE TO THE INFLUENCE OF HEAT

BY

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SOME CHEMICAL AND PHYSICAL CHANGES IN CLAYS DUE TO THE INFLUENCE OF HEAT.

BY

J. M. Knote, Urbana, Ill.

All who have studied clays are aware that the temperature range in which chemical and physical changes may take place, extends from the ordinary atmospheric temperature up to about 1850°C, at which point even the most refractory clay is profoundly affected, both by physical and chemical reactions. The temperature intervals in which reactions of commercial importance occur have been studied with more or less thoroughness, as a survey of the literature will show. Ashley[1], in his studies of the colloidal matter in clays, worked at ordinary atmospheric temperatures. Bleininger[2] heated clays to a point considerably below the temperature of dehydration, and produced reactions of great practical importance. The dehydration of clays has been studied by numerous workers. F. W. Clark[3] and others have attempted to determine the compounds formed when dehydration occurs. Le Chatelier determined the heat changes in some clays when they were heated rapidly from atmospheric temperatures to a high heat. Purdy[4], Bleininger[5] and others have studied the physical and chemical changes produced in clays, and mixtures of clays with other substances, between cone 010 and cone 11. The formation of sillimanite at about 1350°C has been the subject of much experimentation and speculation, and finally the determination of the point of fusion of fire clays has become common.

[1] Trans. A. C. S., Vol. XI.
[2] Trans. A. C. S., Vol. XI.
[3] Bulletin 125, U. S. Geological Survey.
[4] Trans. A. C. S., Vol. IX.
[5] Trans. A. C. S., Vol. X.

It is apparent that very little attention has been paid to what takes place in a clay from the time it begins to lose its combined water until it reaches a point where the reactions of vitrification are started. And there has been no data published on the physical and chemical behavior of fire clays at temperatures above cone 11 and below their fusing point. So the object of this work is to investigate these neglected regions.

The work naturally divides itself into two parts: one an investigation of the behavior of clays below 1000°C, and the other the behavior of refractory clays above 1000°C.

PART I.

INVESTIGATION OF THE CHEMICAL AND PHYSICAL CHANGES THAT OCCUR IN CLAYS AT TEMPERATURES BELOW 1000°C.

Method of Investigation.

Above cone 010, changes in porosity and apparent specific gravity of trial pieces indicate chemical and physical changes, and have been found of great value in studying clays, but below cone 010 these methods of investigation do not apply. The true specific gravity, as determined with the pycnometer, and the chemical properties of the material, would be most likely to indicate and explain any changes which take place.

Determination of True Specific Gravity of High Grade Clays Heated to Temperatures Below 1000°C.

A series of the purer clays was selected to include plastic and non-plastic fire clays, ball clays, kaolins, etc. Shales and red-burning surface clays were not included, as it was desired to avoid as far as possible the effect of the ordinary diluting minerals. The clays were pulverized to pass an eighty mesh sieve. Samples were put into porcelain crucibles and these fired in the laboratory test kiln

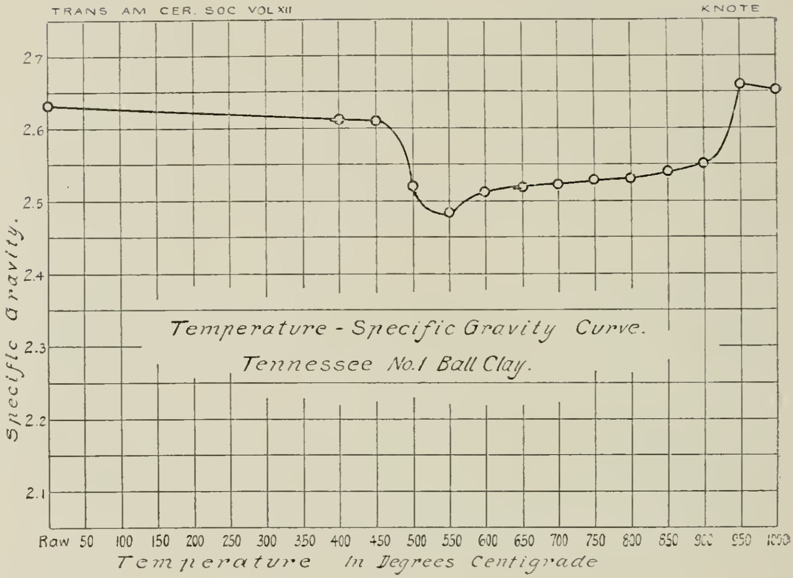
described by Purdy, Vol. IX, Trans. A. C. S. The temperatures were determined by means of a pyrometer, the end of the couple being placed as close as possible to the crucibles to be drawn. A sample of each clay was drawn at intervals of 100°C up to a temperature of 450°C, and after that, every 50°C up to 1000°C. It was not possible to burn all the clays at once, but eight burns were necessary.

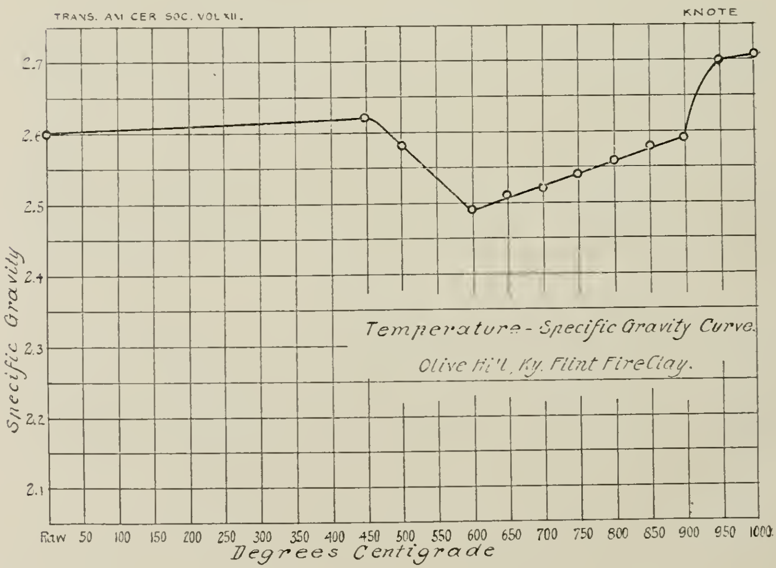
The specific gravity of these samples was determined by means of the pycnometer, or specific gravity bottle. The methods of doing this are described in various text books. Bleininger, Vol. XI, Trans. A. C. S., gives the details of the method and apparatus used in the Ceramic Laboratory of the University of Illinois. The results shown in Table No. 1, and Curves 1 and 2, were obtained by this means.

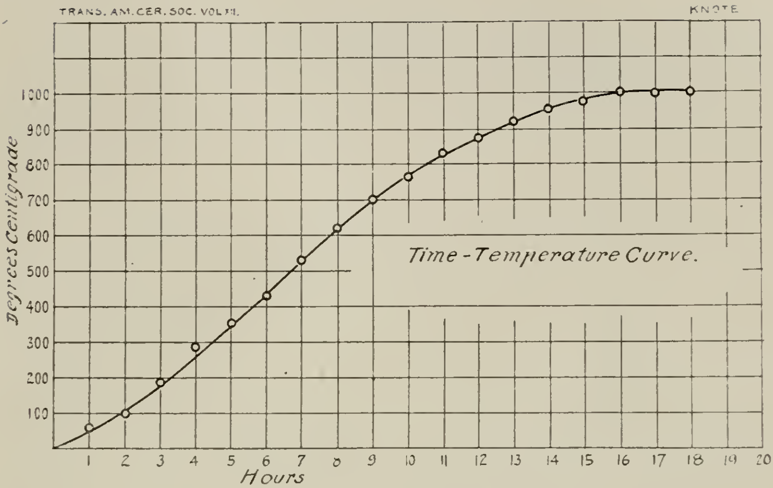
TABLE No. 1.

Pycnometer Results on Various High Grade Clays.

Temperature in Degrees Centigrade	Olive Hill, Ky. Flint Fire Clay	Olive Hill, Ky. Semi-Plastic Fire Clay	Georgia Kaolin	North Carolina Kaolin	Olive Hill, Ky. Plastic Fire Clay	Tennessee No. 1 Ball Clay	Pike's No. 2 Ball Clay	Johnson-Porter No. 9 Tennessee	Woodbridge, N. J. No. 1 Sagger Clay	Paul Clay Co., Akron, Ohio, Fire Clay	J. Poole No. 1 China Clay	Diamond Fire Clay Nelsonville, O.	"Texas Kaolin"
Raw	2.60	2.64	2.60	2.60	2.64	2.61	2.64	2.64	2.64	2.64	2.59	2.64	2.56
450	2.62	2.63	2.59	2.56	2.64	2.61	2.64	2.64	2.62	2.66	2.59	2.62	2.62
500	2.58	2.58	....	2.55	2.55	2.51	2.54	2.54	2.59	2.62	2.53	2.61	2.55
550	2.48	2.51	2.50	2.47	2.52	2.48	2.50	2.53	2.56	2.57	2.47	2.58	2.47
600	2.49	2.51	2.48	2.46	2.52	2.51	....	....	....	....	....	....	....
650	2.51	2.53	2.50	2.49	2.53	2.52	....	....	....	....	....	....	....
700	2.52	2.54	2.51	2.51	....	2.52	....	....	....	....	....	....	....
750	2.54	2.55	2.52	2.52	....	2.53	....	....	....	....	....	....	....
800	2.56	2.56	2.53	2.54	2.55	2.53	....	....	....	....	....	....	....
850	2.58	2.57	2.55	2.55	....	2.54	....	....	....	....	....	....	2.52
900	2.59	2.59	2.55	2.59	2.59	2.55	2.56	2.55	2.56	2.54	2.50	2.51	2.52
950	2.70	2.70	2.70	2.72	2.66	2.66	2.59	2.61	2.59	2.64	2.52	2.64	2.55
1000	2.70	2.70	2.69	2.72	2.63	2.65	2.66	2.66	2.66	2.69	2.61	2.64	2.57


TRANS AM CER. SOC VOL XII
KNOTE
Temperature - Specific Gravity Curve.
Tennessee No. 1 Ball Clay.
Specific Gravity.
2.7
2.6
2.5
2.4
2.3
2.2
2.1
Raw 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Temperature In Degrees Centigrade


TRANS. AM CER SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Olive Hill, Ky. Flint FireClay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
Raw 50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
Degrees Centigrade



Discussion of Pycnometer Data.

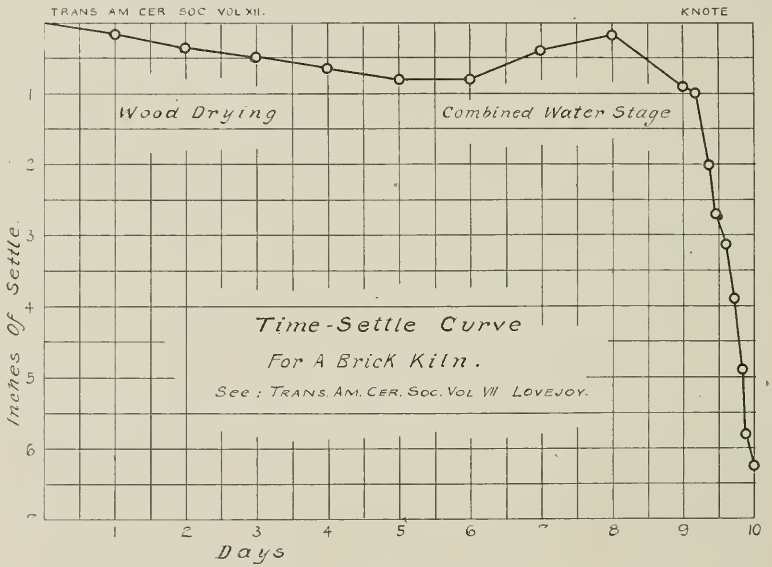
It is significant that the curves for such a large variety of clays are so similar. There may be essential differences in the behavior of various clays, but if this is true, we failed to discover it. The only difference we can see is that the non-plastic clays seem to reach a higher specific gravity at 950°—1000° C than do the plastic clays. An inspection of the results given in Part 2 of this paper will also indicate that this is true in general. The notable exceptions are in the case of Poole's No. I China Clay and the fire clay from the Diamond Clay Co. There is no doubt that the specific gravity of a burned clay is the resultant of several factors, but it seems that the physical condition is one of these.

Lovejoy's Settle Curves.

Lovejoy (Vol. VII, Trans. A. C. S.) made careful measurements of the settle in brick kilns, from the time the fires were lighted until the kiln was finished, and found that the height of the brick in the kiln increased at about the temperature of dehydration, indicating an increase in

volume of the brick. This would seem to confirm our results, as a decrease in true specific gravity would give an increased volume.

Curve No. 3 is one of the many which Mr. Lovejoy obtained.



Work to Determine the Causes of the Specific Gravity Changes Below 1000° C.

It is evident that an investigation of the chemical properties of the material is necessary to determine the character of the changes indicated by the specific gravity determinations. It has been known for a long time that weakly ignited clays when mixed with slaked lime and water are pozzuolanic in character and will set and harden. Second, it has been pointed out that dehydrated clay is much more soluble in acid than the raw material. These are the reactions which were used to investigate the character of dehydrated clay.

Clay Investigated.

It would have been desirable to investigate a series of clays, but since we could not do that a very pure plastic fire clay from Olive Hill, Ky., was used. It had about the following composition:

Silica	47.08
Alumina	39.86
Oxide of Iron	0.88
Lime	Tr.
Magnesia	Tr.
Potash	Tr.
Soda	Tr.
Loss on Ignition	12.34
Cone of Fusion	34.

This clay is described by Greaves-Walker, Trans. A. C. S., Vol. IX.

Behavior with Lime and Water.

Samples of finely pulverized clay were ignited, one to 600°C, the second to 800°C, a third to 950°C and another to 1050°C. These were mixed with 33⅓% slaked lime by grinding dry in a ball mill. The mixed material was made plastic with water and moulded into the regulation tensile test briquettes. These were kept in a damp cellar for twenty-four hours, and then immersed in water for twenty-eight days. At the end of this time, the samples which had been burned to 600°C and 800°C averaged 160 pounds per square inch, the 950°C sample 110 pounds per square inch, but the one which had been burned to 1050°C slaked down, giving zero tensile strength. This shows that the hydraulic properties are immediately lessened as a result of the change which produces the increase of specific gravity. To determine just how rapidly the clay loses its hydraulic properties a variety of clays should be tested. Our work does not show this as completely as it should, but from the work we did, a clay and lime mixture seems to behave just as a Roman cement, which is not surprising.

Behavior of Dehydrated Clay and Lime Mixtures When Subjected to High Pressure Steam.

The same mixtures which were tested for hydraulicity were put into a small steam cylinder, which was used for hardening sand-lime mixtures, and subjected to steam at 110 pounds pressure, for eight hours. The briquettes made from clay, calcined below 950°C, gave an average tensile strength of 140 pounds per square inch, and those which were heated above 950°C averaged 290 pounds per square inch. The latter briquettes were much denser and harder than those of the lower calcined material.

Effects of Chemical Reagents on Clays Calcined at Various Temperatures.

The Olive Hill plastic clay mentioned before was used for this experiment also. Three samples were used: (1) raw, (2) calcined to 600°C, (3) calcined to 1000°C. These were boiled four hours with Na_2CO_3 solution, 250 grams Na_2CO_3 per liter, with very little effect on any of them. Samples of the same material were then repeatedly boiled with 1:3 HCl solution, the residue being treated with dilute alkali solution containing 1 gram NaOH and 3 grams Na_2CO_3 per 50 c. c. (See Chemical Examination of Pozzuolane Material, Bulletin 3, Geological Survey of Ohio, Fourth Series, p. 111.)

This treatment extracted 6% from the raw clay, 44% from that calcined to 600°C, and 5% from the 1000°C sample.

This shows the very marked difference in solubility of the material calcined at different temperatures. Edgar ball clay was tried in the same way and gave about the same result, except 70% was extracted from the 600° C. sample.

Summary of Results.

(1) When the chemically combined water is expelled from a clay, compounds are formed which have a lower specific gravity than the raw clay itself.

(2) There is a sudden increase in specific gravity about 950°C, at which point Le Chatelier reported an exothermic reaction.

(3) Essentially the same curve was obtained for all clays tested.

(4) With two or three exceptions, the non-plastic clays reached slightly higher specific gravity at 950°—1000°C than the plastic clays did.

(5) Dehydrated clays which have not been heated above 900°C are pozzuolanic in character, but lose this property rapidly if heated above 950°C.

(6) Clays heated above 950°C, when mixed with lime and water and subjected to high pressure steam, give a very much stronger body than similar mixtures of clay which were heated below 950°C.

(7) Raw clays and clays heated above 950°C are not attacked appreciably by Na_2CO_3, and but slightly by HCl. Dehydrated clays heated to temperatures below 900°C are not attacked by Na_2CO_3, but are strongly attacked by HCl.

(8) The residue after treatment of the dehydrated clay with HCl is but slightly pozzuolanic in character.

Conclusions.

Our data does not show the water content of a clay in its various stages of dehydration, but we know from the work of others that the water does not all leave at once, and a part often remains until the temperature advances considerably. It would be impossible to state just what is formed as products of dehydration, without taking this fact into consideration. However, we think we have evidence to disprove the general idea that Al_2O_3 $2SiO_2$ $2H_2O$ breaks down into Al_2O_3 $SiO_2+SiO_2+2H_2O$. So far as we can find out, there is no positive evidence to support this view, but it is based on the fact that sillimanite (Al_2O_3 SiO_2) is stable at high temperatures, while other silicates of alumina are less so. These cannot be the compounds

really formed by dehydration, as the experimental facts given above cannot be accounted for on this basis.

We wish to suggest the following as an attempt to explain the facts noted. $Al_2O_3\ 2SiO_2\ 2H_2O$ breaks up to form $Al_2O_3\ SiO_2 + Al_2O_3\ 3SiO_2 + 2H_2O$ which has a lower specific gravity than the $Al_2O_3\ 2SiO_2\ 2H_2O$.

If this change takes place in the clays examined it is fairly reasonable to assume that the same will occur in any clay, since the specific gravity changes are similar in all cases.

What causes the specific gravity to immediately increase after reaching a minimum we can not explain, unless it is the expulsion of the remaining water.

We have not proven what causes the increase of specific gravity at 950°C, but hope to have some data to offer a little later. It might be due either to the formation of an isomeric compound or to the combination of silicates to produce a new compound. Either reaction might evolve heat. We suggest a combination of the above mentioned silicates to form $Al_2O_3\ 2\,SiO_2$, but as stated before, we have not proven it. The behavior of the clay when ignited to 1000°C, mixed with lime and water and subjected to high pressure steam, is a point against the formation of an isomeric compound. Also numerous writers have spoken of $Al_2O_3\ 2SiO_2$ breaking up at high temperatures under the action of fluxes, but this statement may not be based on established facts. An acid silicate and a basic silicate are known to be formed at high temperatures, and the only question is as to what breaks up or changes when they are produced.

The fact that the non-plastic clays seem to acquire a higher specific gravity than the plastic clays is probably due to the difference in the physical condition of the clays themselves.

PART II.

This part of the investigation was devoted to a study of the physical behavior of typical fire clays in the temperature interval between cone 010 and cone 23. It was originally intended to carry every clay to its fusing point, but we were unable to do this on account of an accident to the furnace we were using.

Method of Procedure.

The nonplastic clays were pulverized to about 8 mesh and then wet-ground in a ball mill for three hours, after which all of them were plastic enough to be molded into briquettes quite readily. The charge in the mill was so adjusted that a good assortment of sizes of grains was secured, which ran 10 mesh and finer. The plastic clays were dry-ground, wet, wedged, and molded into briquettes. The briquettes were burned in a coke-fired test kiln to cone 11, a draw being taken at the temperatures indicated on the following curve sheets. For temperatures above cone 11, the oil-fired test kiln described elsewhere in this volume, was used.

Duration of the Heat Treatment.

All the briquettes were first burned in the coke-fired test kiln, the temperature being raised gradually, cone 11 being reached in 36 hours. For the temperatures above cone 11 the calcined briquettes were put in the oil-fired kiln. This was fired so as to reach 550° C. in one hour, cone 11 in two hours, cone 15 in four hours, cone 20 in five hours, and cone 23 in six hours. The burns varied from this schedule somewhat, but not enough to make any essential difference. All the clays were carried to a given temperature at the same time.

Tests After Burning.

The apparent specific gravity, porosity and shrinkage of the briquettes were obtained in the usual way. The following curves and tables show the results.

Olive Hill, Ky., Flint Fire Clay.

This clay is from the mines of the Olive Hill Fire Brick Co. at Olive Hill, Carter County, Kentucky. The clay deposits of this region have been described by Greaves-Walker, Vol. IX Trans. A. C. S. The clay at Olive Hill is at the level of the Maxville limestone, just at the top of the Sub-Carboniferous or Mississippian strata.

The following analysis is typical:

SiO_2	43.80
Al_2O_3	40.71
Fe_2O_3	0.81
CaO	0.96
MgO	0.13
Volatile matter	13.43
Cone of fusion	34-35

Under the microscope in thin sections, the clay is seen to be made up almost entirely of a structureless ground mass, which has very little effect on polarized light. Embedded in the ground mass are a very few rounded grains of quartz, and a small amount of a micaceous mineral, a few grains of rutile, zircon, etc. There are areas which represent pebbles which are now entirely decomposed to a substance differing from the material in which they lie, in consequence of their greater richness in micaceous particles.

RESULTS.

The specific gravity curve proves to be practically a straight line up to cone 23, which is a most unusual condition. Another noteworthy fact is that the clay decreases in porosity between cones 05 and 11 without any change in specific gravity. The high fire shrinkage seems to be characteristic of some flint clays, but the data which follows shows that it is not true, by any means, of all of them.

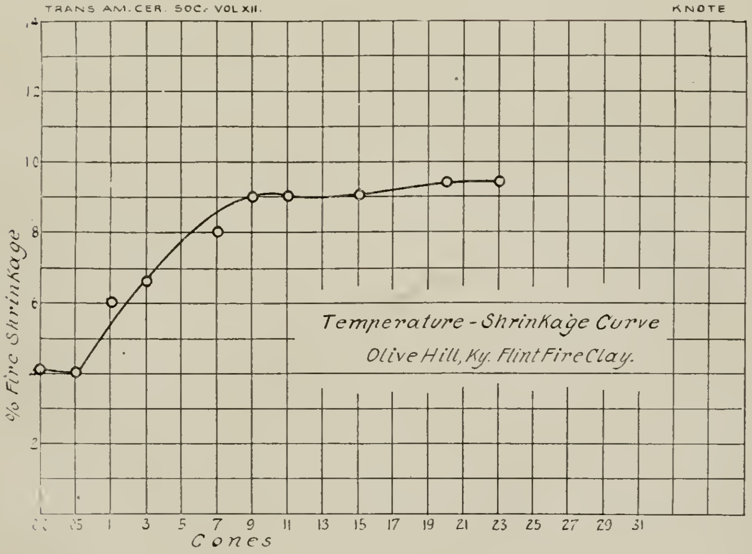
The microscopical examination failed to show any crystalline structure in this flint clay, or in any other flint clay examined. Under polarized light, the ground mass behaved as an amorphous substance.

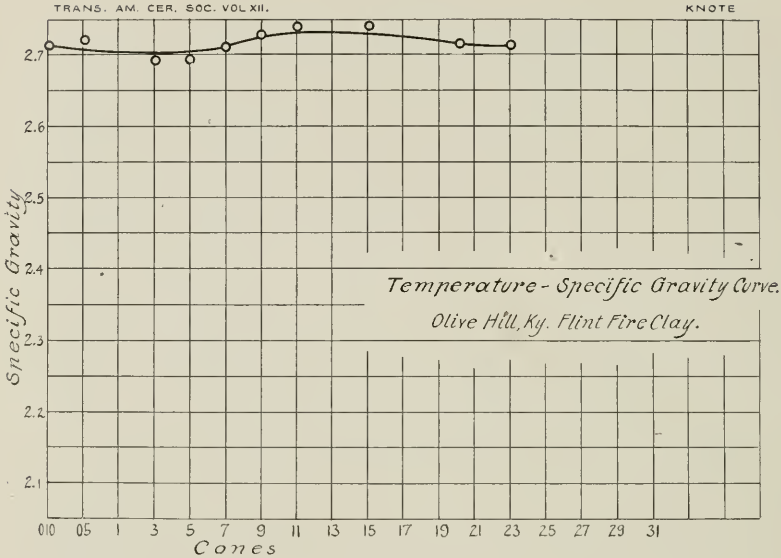
TABLE I.

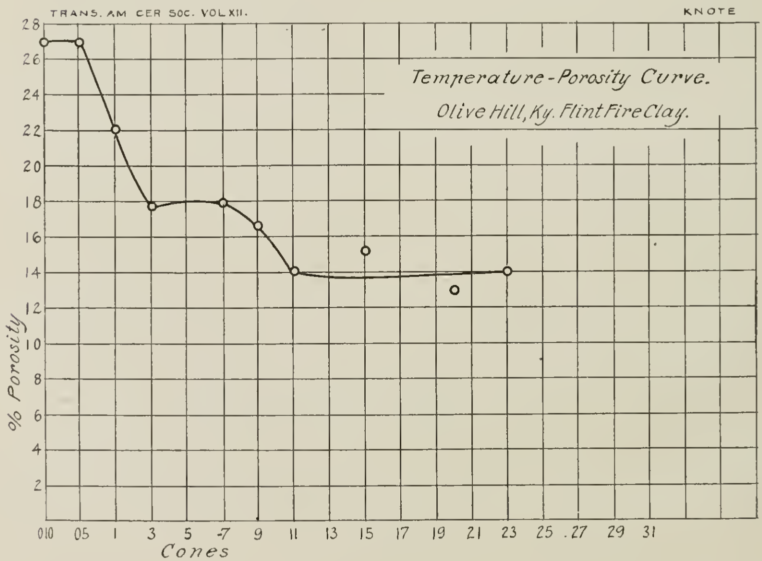
OLIVE HILL FLINT FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	4.0	2.71	26.4
2	05	4.0	2.72	26.4
3	1	6.0	2.69	22.0
4	3	6.5	2.69	17.8
5	5	...	....	....
6	7	8.0	2.71	18.0
7	9	9.0	2.73	16.7
8	11	9.0	2.74	14.0
9	15	9.0	2.74	16.0
10	20	9.5	2.71	13.5
11	23	9.5	2.71	14.0




TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Olive Hill, Ky. Flint Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

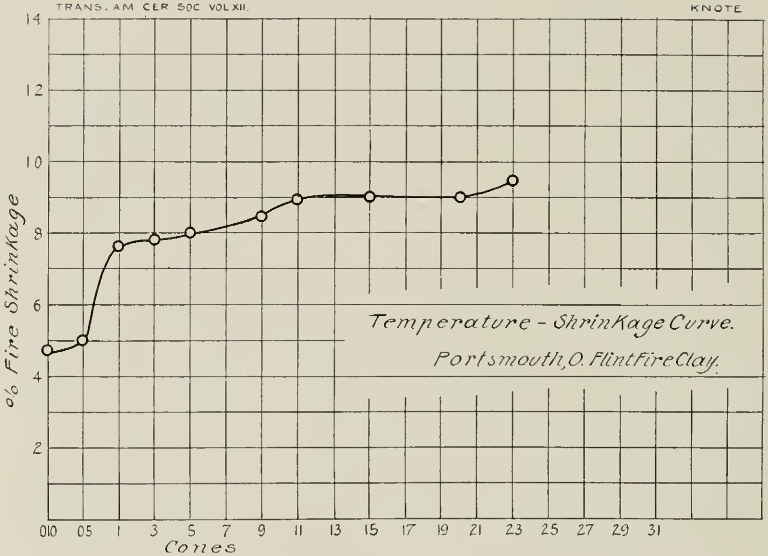

TRANS. AM CER SOC. VOL XII.
KNOTE
Temperature - Porosity Curve.
Olive Hill, Ky. Flint Fire Clay.
% Porosity
28
26
24
22
20
18
16
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

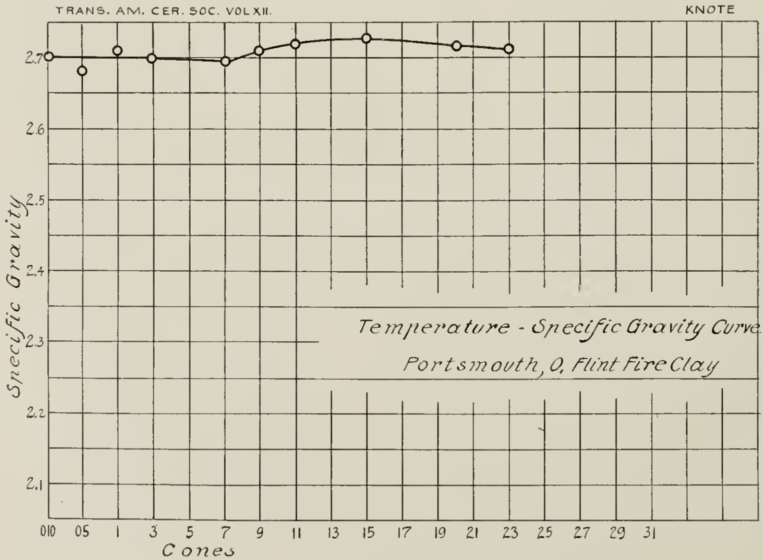
PORTSMOUTH, O., FLINT FIRE CLAY.

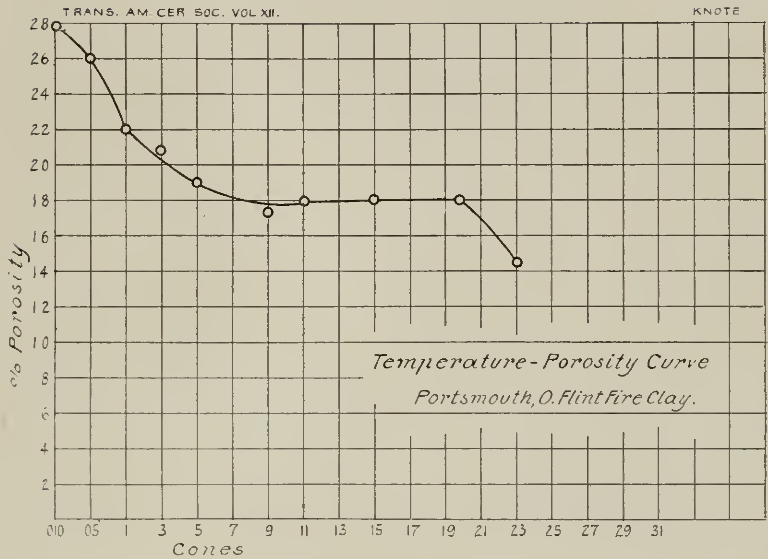
The geological horizon, occurrence, and properties of this clay are the same as those of the specimens from Olive Hill, Ky. It is rather noteworthy that, considering the great variation of the flint clays even in a restricted area, two clays from such widely separated deposits should be so nearly identical, even if they do occur at the same horizon.

PORTSMOUTH, O., FLINT FIRE CLAY.
Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	4.48	2.70	28.0
2	05	5.0	2.68	26.3
3	1	7.7	2.71	22.1
4	3	7.9	2.70	21.0
5	5	8.0	2.69	19.2
6	7	...	....	....
7	9	8.5	2.71	17.6
8	11	9.0	2.72	18.0
9	15	9.0	2.73	18.0
10	20	9.0	2.72	18.0
11	23	9.5	2.71	14.5
12	..	...	....	....


TRANS. AM CER SOC VOL XII.
KNOTE
Temperature - Shrinkage Curve.
Portsmouth, O. Flint Fire Clay.
% Fire Shrinkage
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Portsmouth, O. Flint Fire Clay
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones



McKeesport, Pa., Flint Fire Clay.

This clay was supplied by Mr. J. P. McIntyre, of McKeesport, Pa., from a tract in Bell Township, Clearfield County, Pa. It is marked McKeesport Clay to distinguish it from another clay also from Clearfield County, Pa. Nothing is known of its exact occurrence, chemical or mineral constitution. It was rather dark in color and had the usual physical properties of a flint clay.

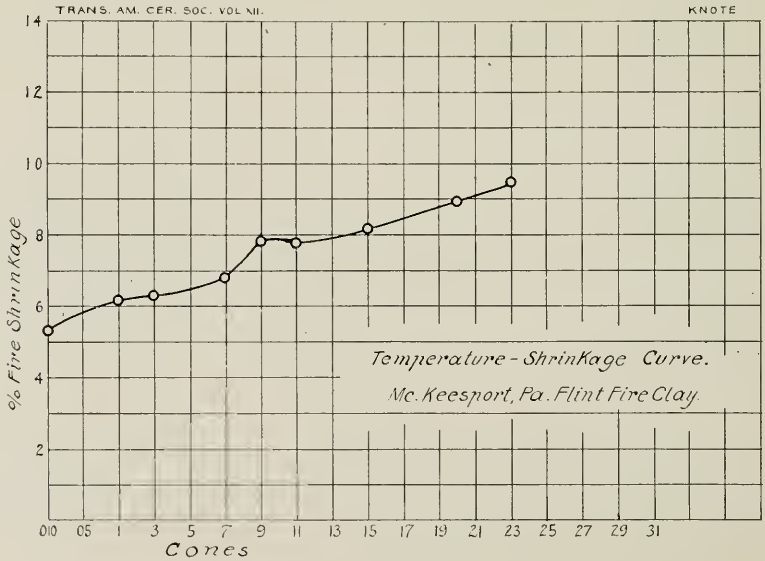
RESULTS.

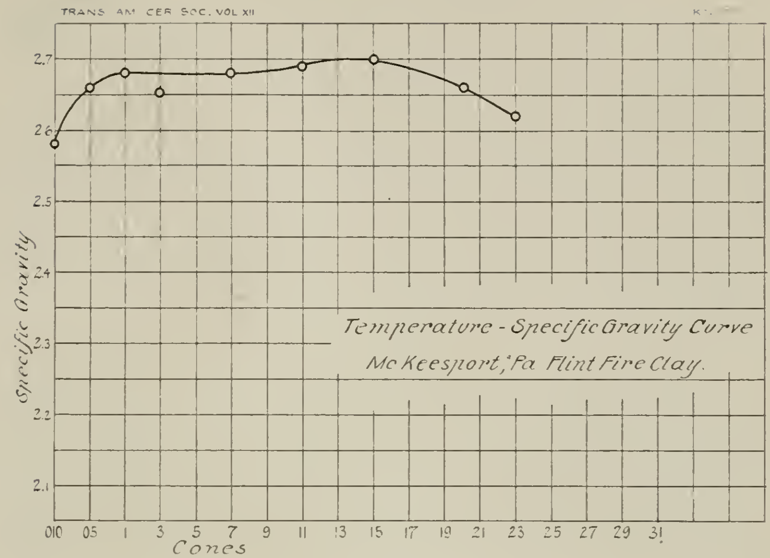
The specific gravity begins to drop about cone 15, which distinguishes it from the Olive Hill and Portsmouth clays. The porosity and shrinkage seem to change gradually but almost continuously.

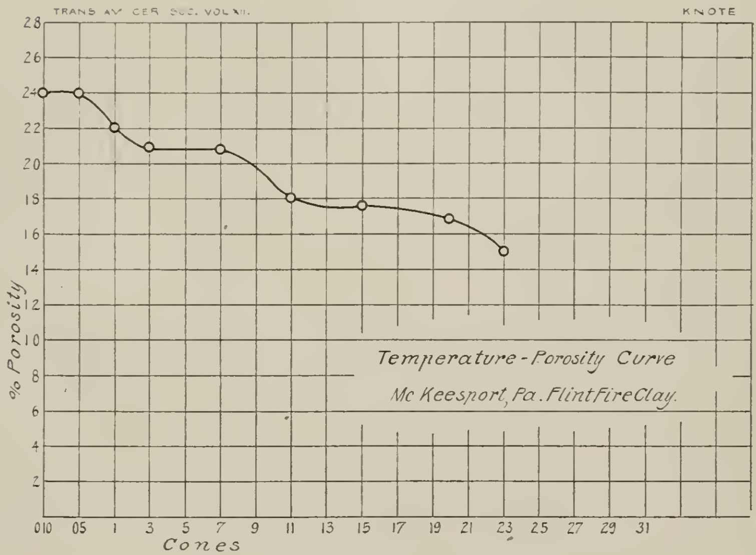
McKEESPORT, PA., FLINT FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed In Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	5.3	2.58	24.0
2	05	6.1	2.66	24.0
3	1	6.1	2.68	22.0
4	3	6.2	2.65	21.0
5	5	...	....	....
6	7	6.8	2.68	21.0
7	9	...	....	....
8	11	7.9	2.69	18.0
9	15	8.2	2.70	17.8
10	20	9.0	2.66	16.5
11	23	9.5	2.62	15.5




TRANS AM CER SOC. VOL XII
Temperature - Specific Gravity Curve
Mc Keesport, Pa Flint Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS AM CER SOC. VOL XII.
KNOTE
Temperature - Porosity Curve
Mc Keesport, Pa. Flint Fire Clay.
% Porosity
28
26
24
22
20
18
16
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

Clearfield County, Pa., Flint Fire Clay.

This clay is being used at the present time for the manufacture of first class refractory wares. As nearly as we can determine from survey reports, it occurs at the level of the Mercer coals in the Pottsville conglomerate. Under the microscope it shows a little more quartz than the Olive Hill clay, but the ground mass which makes up the bulk of the material seems to be the same and affects polarized light very little. The quartz grains nearly all exhibit strain as though derived from a schist.

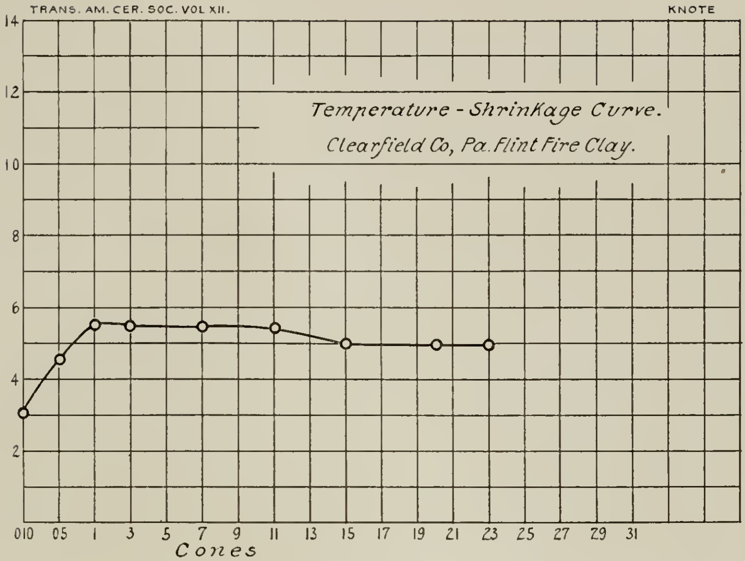
RESULTS.

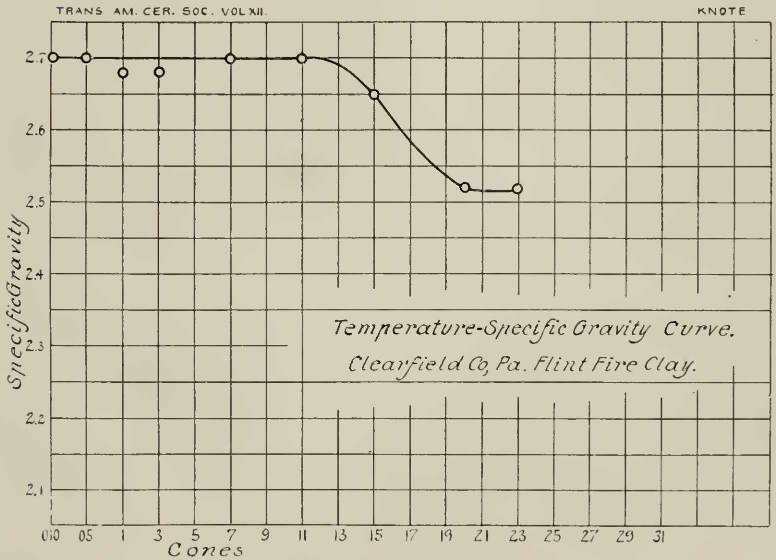
The clay shows itself to be of quite different character from the Olive Hill clay. The specific gravity takes a decided drop about cone 13, but the porosity remains unchanged to a much higher temperature. The fire shrinkage is not high, and the clay seems to swell slightly as the specific gravity drops. This is a condition not frequently met with.

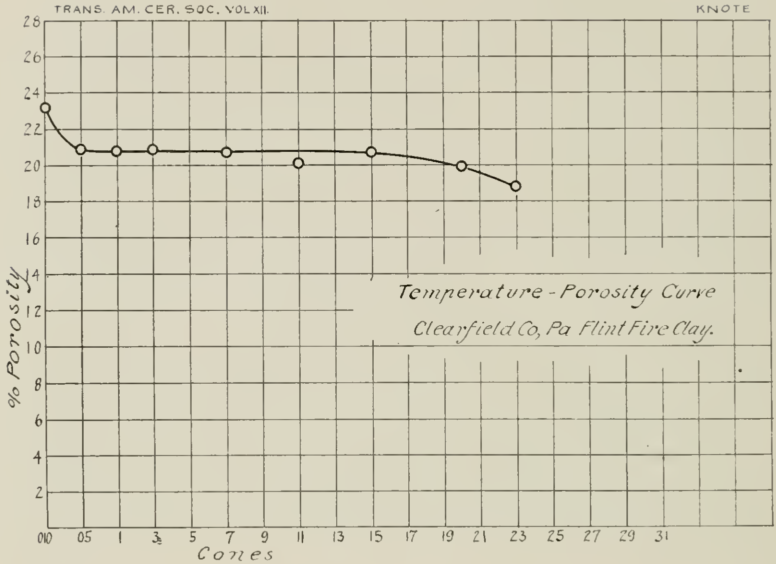
CLEARFIELD CO., PA., FLINT FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	3.0	2.70	23.0
2	05	4.3	2.70	21.0
3	1	5.6	2.68	21.0
4	3	5.6	2.68	21.4
5	5	...	....	....
6	7	5.6	2.70	21.4
7	9	...	....	....
8	11	5.6	2.70	20.1
9	15	5.0	2.65	21.0
10	20	5.0	2.52	20.0
11	23	5.0	2.52	18.5


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Shrinkage Curve.
Clearfield Co, Pa. Flint Fire Clay.
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS AM. CER. SOC. VOL XII.
KNOTE
Temperature-Specific Gravity Curve.
Clearfield Co, Pa. Flint Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones



Savage Mt., Md., Flint Fire Clay.

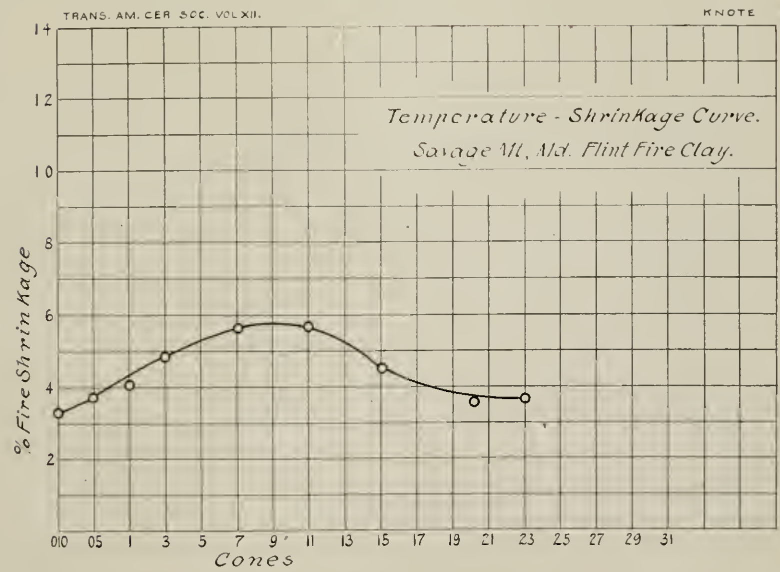
This clay occurs at the same horizon ascribed to the Clearfield County, Pa., clay, namely, the level of the Mercer coals. It is very similar to the Pennsylvania clay, as the curves show. Occasional pieces show a well marked breccia structure, with irregular sharp edged pieces of various sizes imbedded in a cementing material, which must be very similar in composition to the pieces themselves.

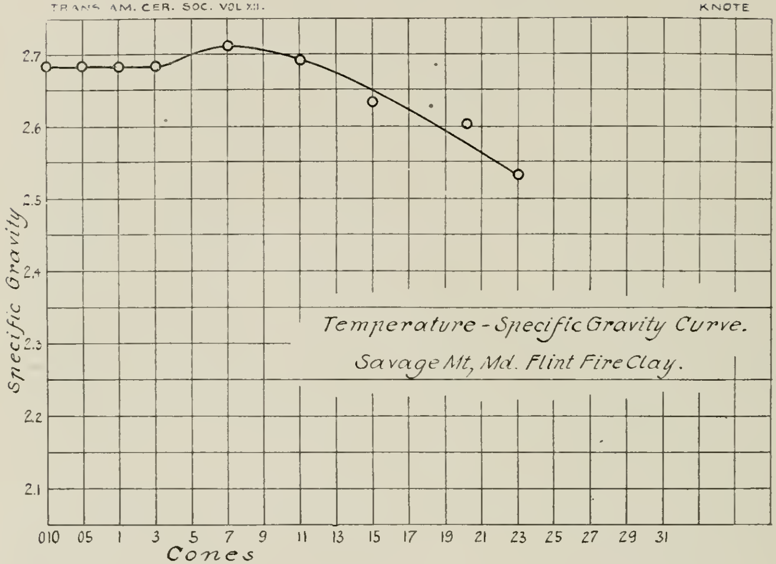
RESULTS.

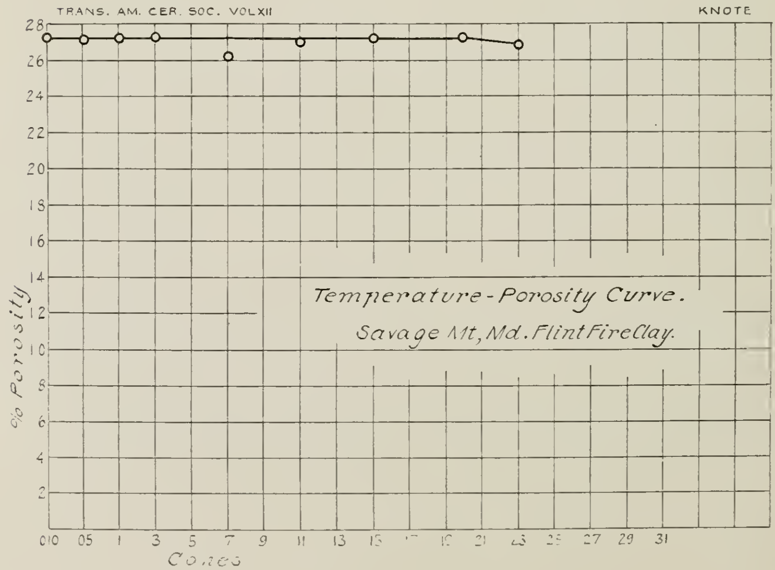
A drop in specific gravity about cone 13, with no decrease in porosity accompanying it, but an increase in volume being shown by the shrinkage measurement, are the same features pointed out in regard to the Pennsylvania clay. This is the second case of flint clays occurring at the same horizon, exhibiting about the same properties, even if separated by a distance of many miles.

SAVAGE MT. FLINT FIRE CLAY.
Data Obtained on Burned Briquettes.

No.	Heat Treatmenet Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	3.3	2.68	28.0
2	05	3.8	2.68	28.0
3	1	4.0	2.68	28.0
4	3	4.8	2.68	28.0
5	5	...	....	....
6	7	5.6	2.71	26.0
7	9	...	....	....
8	11	5.6	2.69	28.0
9	15	4.4	2.63	28.0
10	20	3.5	2.60	28.0
11	23	3.6	2.53	28.0




TRANS. AM. CER. SOC. VOL XII.
KNOTE
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones
Temperature-Specific Gravity Curve.
Savage Mt, Md. Flint Fire Clay.


TRANS. AM. CER. SOC. VOL XII
KNOTE
% Porosity
28
26
24
22
20
18
16
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15
27 29 31
Cones
Temperature-Porosity Curve.
Savage Mt, Md. Flint Fire Clay.

Mineral City, Ohio, Flint Fire Clay.

This clay occurs higher up in the geological scale than the clays described, namely, at the level of the Lower Kittanning clay and coal. It shows much more quartz, when examined by the microscope, than the other clays do. The quartz is characterized by very sharp edges, which would indicate a residual origin.

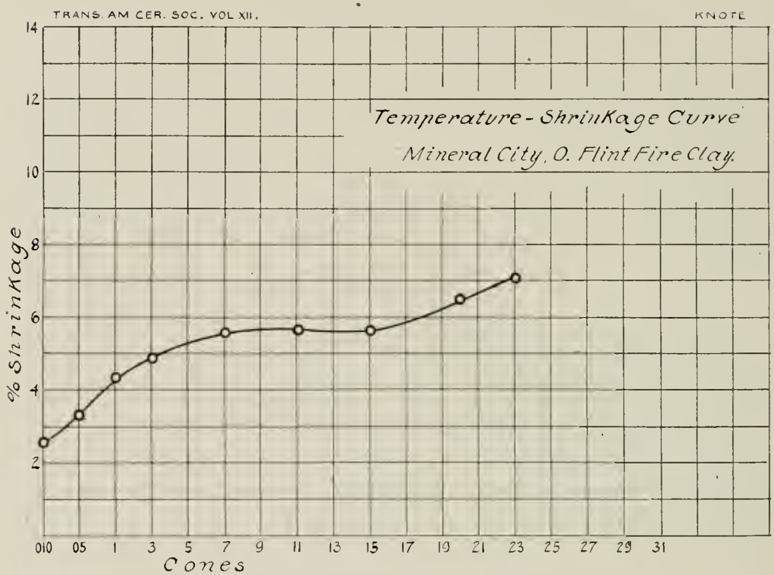
RESULTS.

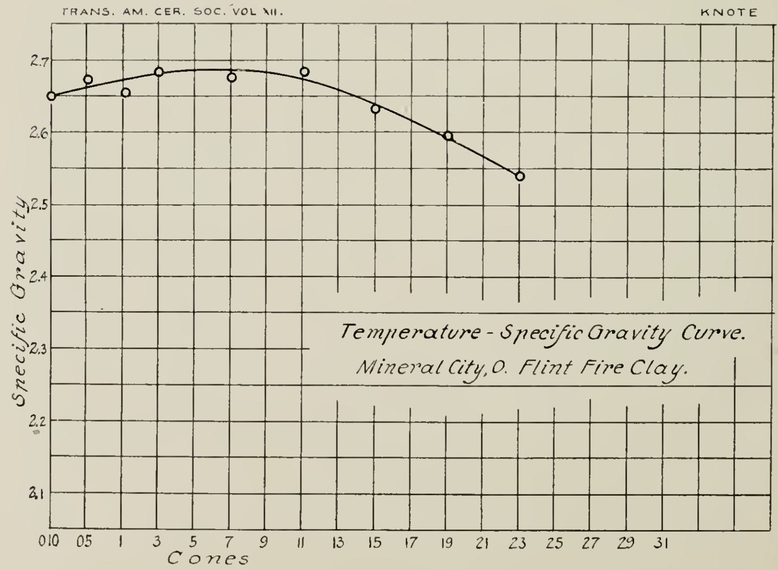
The data shows a drop in specific gravity at about the same temperature at which the phenomenon occurred in the two preceding clays, but the porosity begins to decrease about cone 11. With the decrease in porosity also comes an increase in shrinkage. This is the only flint clay examined whose physical properties changed, as we expected from a study of the plastic clays.

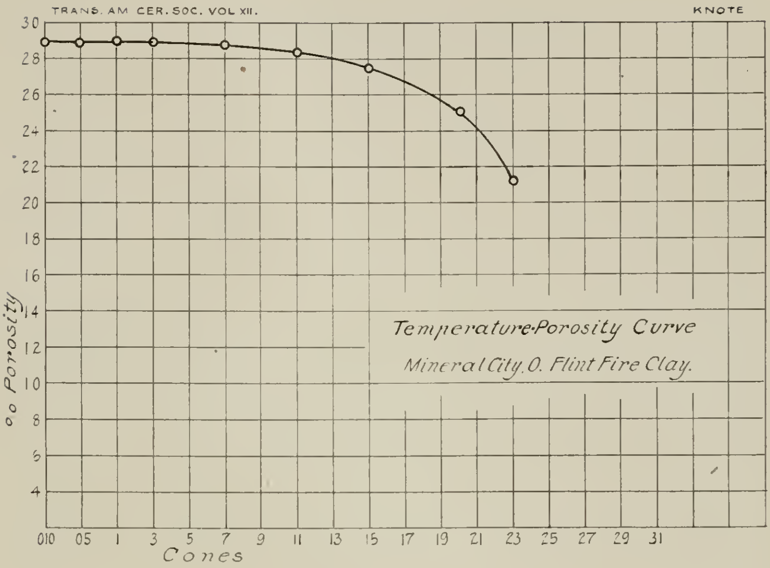
MINERAL CITY, O., FLINT FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	2.5	2.65	29.0
2	05	2.8	2.67	29.0
3	1	4.3	2.65	29.0
4	3	4.8	2.68	29.0
5	5	...	....	....
6	7	5.6	2.67	28.4
7	9	...	....	....
8	11	5.6	2.68	28.0
9	15	5.6	2.63	27.5
10	20	6.6	2.58	25.0
11	23	7.0	2.54	21.0


TRANS. AM CER. SOC. VOL XII.
KNOTE
Temperature - Shrinkage Curve
Mineral City, O. Flint Fire Clay.
% Shrinkage
Cones
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Mineral City, O. Flint Fire Clay.
Specific Gravity
Cones
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31



Clearfield County, Pa., Plastic Fire Clay.

This clay is not a typical plastic clay, but seems to be more of the semi-flint. It could be regarded as one of the transition clays between the flint and plastic varieties.

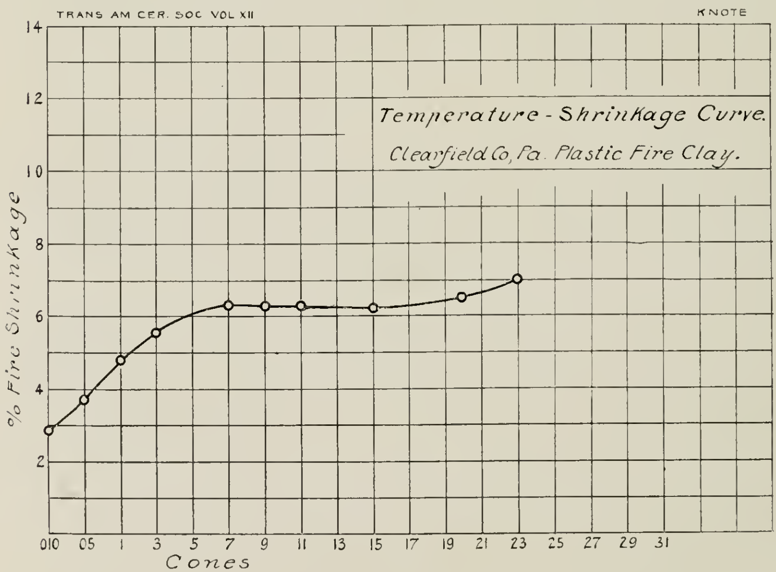
RESULTS.

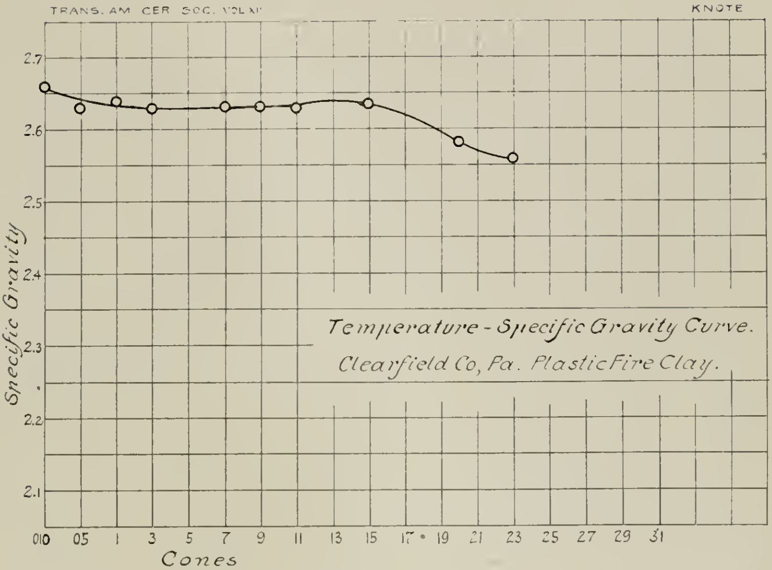
Its behavior is much more that of a flint clay than it is of a plastic. The drop in porosity is greater than that of any flint clay examined, but not as great as that of the plastic clays.

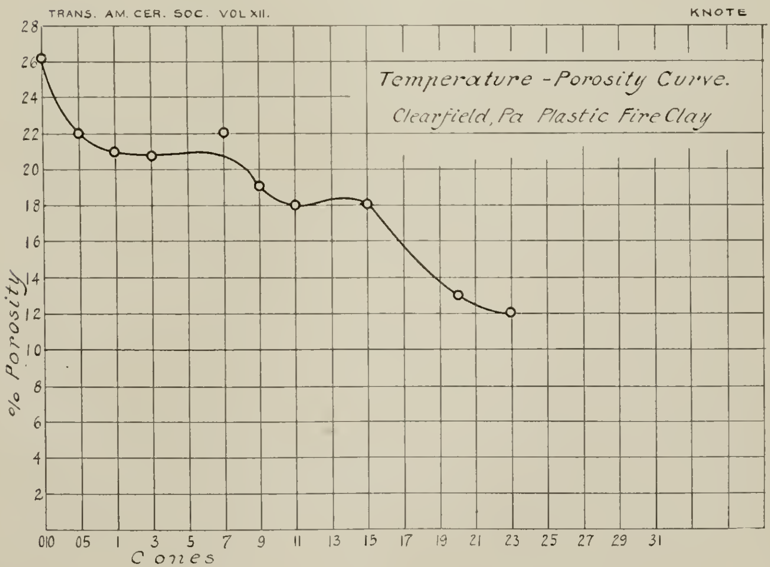
CLEARFIELD CO., PA., PLASTIC FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	2.8	2.66	26.0
2	05	3.7	2.63	22.0
3	1	4.9	2.64	21.0
4	3	5.6	2.63	21.0
5	5	...	....	....
6	7	6.2	2.64	22.0
7	9	...	....	....
8	11	6.2	2.64	18.0
9	15	6.1	2.64	18.0
10	20	6.5	2.58	13.0
11	23	7.0	2.56	12.0




TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Clearfield Co, Pa. Plastic Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Porosity Curve.
Clearfield, Pa Plastic Fire Clay
% Porosity
28
26
24
22
20
18
16
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

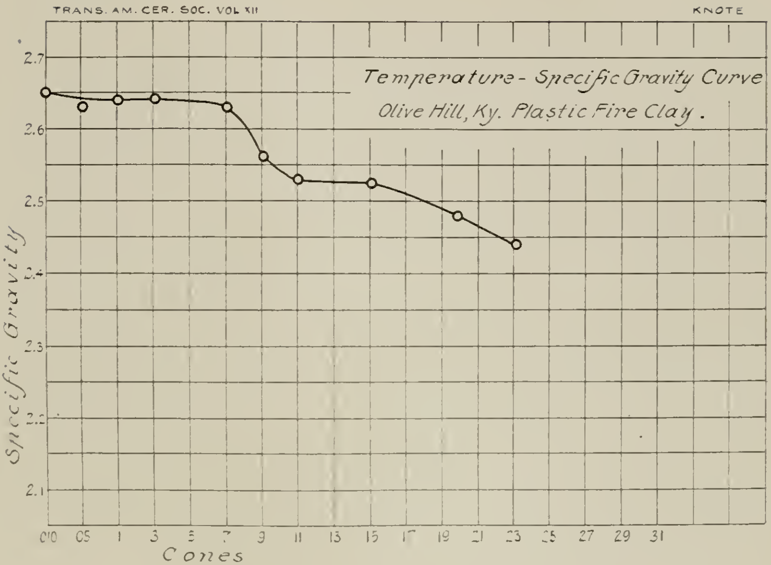
Olive Hill, Ky., Plastic Fire Clay.

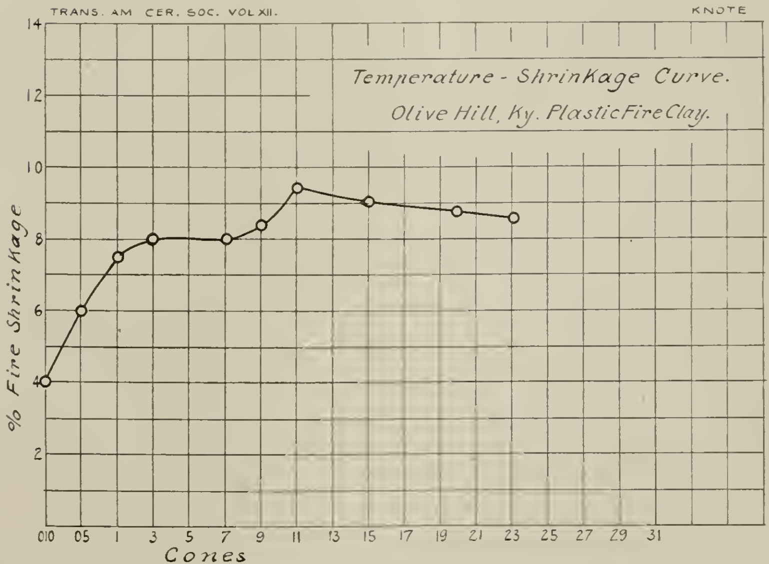
This is a remarkable plastic clay. It does not resemble any of the preceding clays in the least, so far as its physical properties are concerned, but it has very nearly the same chemical composition as the Olive Hill flint clay. Its occurrence and properties are described by Greaves-Walker in Vol. IX, Trans. A. C. S., it being known locally as the Blankenship plastic clay. Occurring in the same vein with a flint clay of almost identical chemical composition, and almost the same cone of fusion, it serves to eliminate most of the factors which have been suggested to explain the difference between plastic and non-plastic clays.

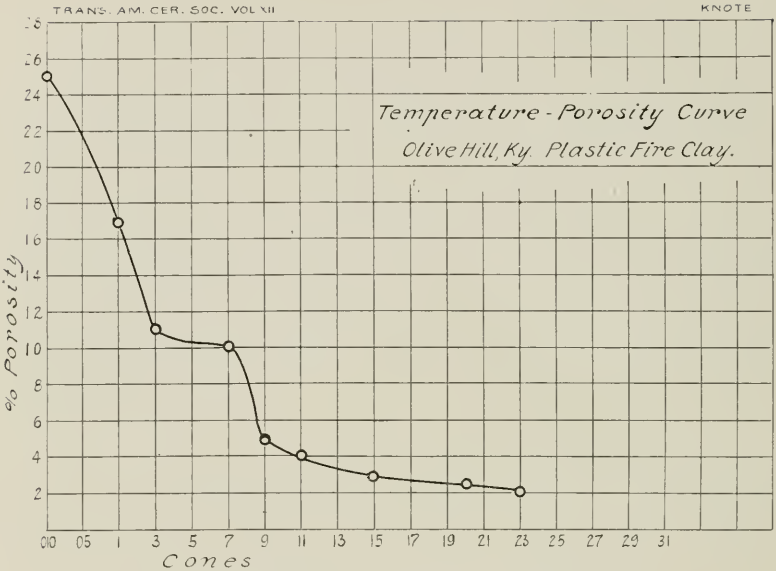
OLIVE HILL, KY., PLASTIC FIRE CLAY.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	4.1	2.65	25.0
2	05	5.8	2.64	17.0
3	1	7.5	2.64	14.4
4	3	8.0	2.64	11.0
5	5	...	....	....
6	7	8.0	2.63	11.0
7	9	8.6	2.56	5.0
8	11	9.3	2.54	4.0
9	15	9.0	2.54	3.0
10	20	8.8	2.48	2.5
11	23	8.6	2.44	2.0


TRANS. AM. CER. SOC. VOL XII
KNOTE
Temperature - Specific Gravity Curve
Olive Hill, Ky. Plastic Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Shrinkage Curve.
Olive Hill, Ky. Plastic Fire Clay.
% Fire Shrinkage
14
12
10
8
6
4
2
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

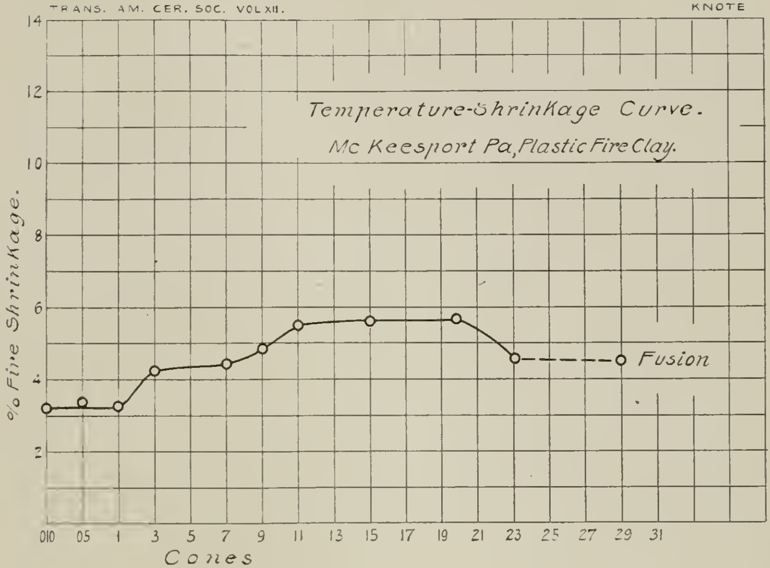


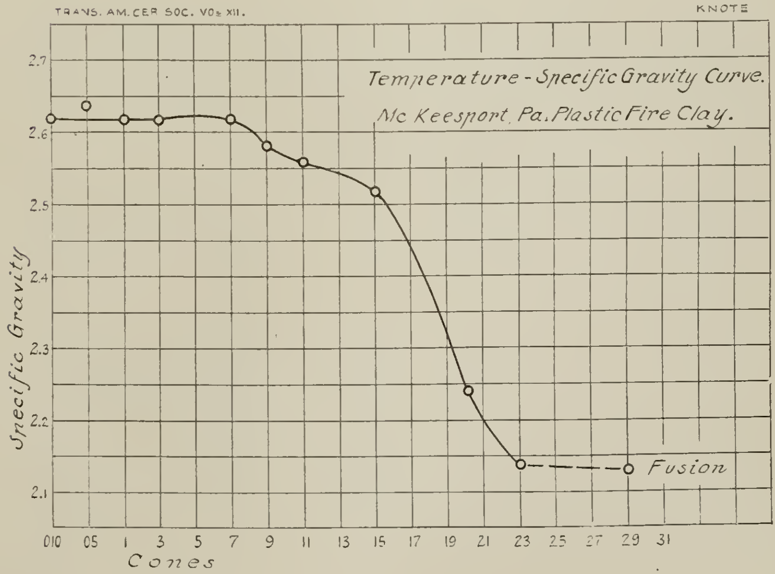
McKeesport, Pa., Plastic Fire Clay.

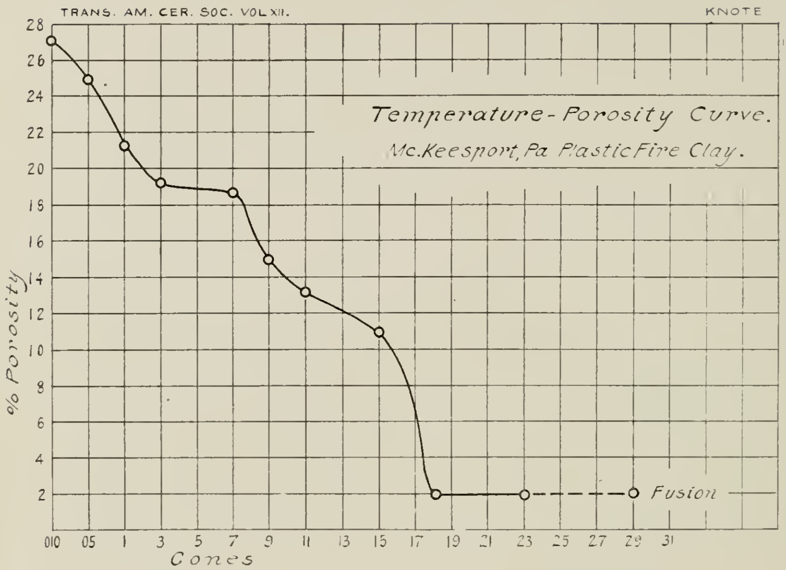
This clay is from the same locality as the flint clay listed as McKeesport, Pa., flint clay. It presents nothing out of the ordinary except that in the raw condition it has more of a shale structure than that of a typical fire clay.

McKEESPORT, PA., PLASTIC FIRE CLAY.
Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	3.1	2.62	27.1
2	05	3.2	2.64	25.0
3	1	3.1	2.62	21.6
4	3	4.1	2.62	19.2
5	5	...	....	....
6	7	4.3	2.62	18.7
7	9	4.9	2.58	15.3
8	11	5.3	2.56	13.4
9	15	5.6	2.52	11.0
10	20	5.6	2.24	2.0
11	23	4.3	2.14	2.0


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature-Shrinkage Curve.
Mc Keesport Pa, Plastic Fire Clay.
% Fire Shrinkage.
14
12
10
8
6
4
2
Fusion
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS. AM. CER. SOC. VOL XII.
KNOTE
Temperature - Specific Gravity Curve.
Mc Keesport, Pa. Plastic Fire Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
Fusion
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

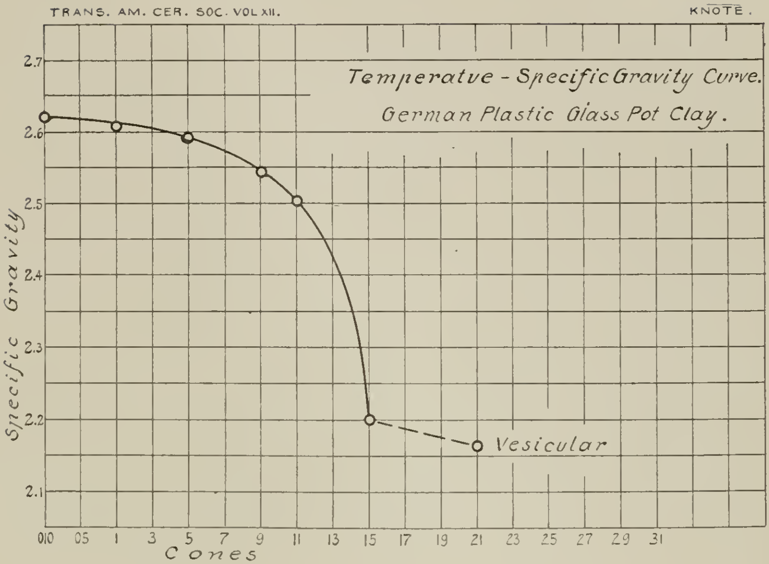


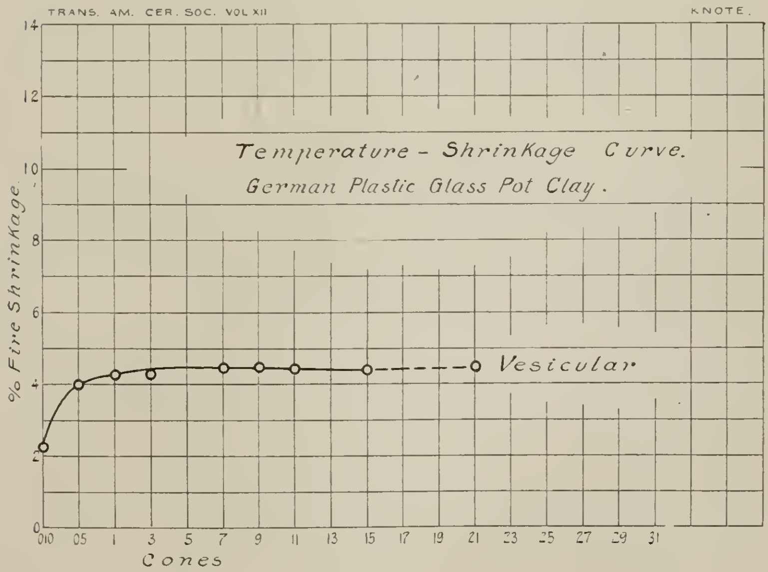
German Plastic Glass Pot Clay.

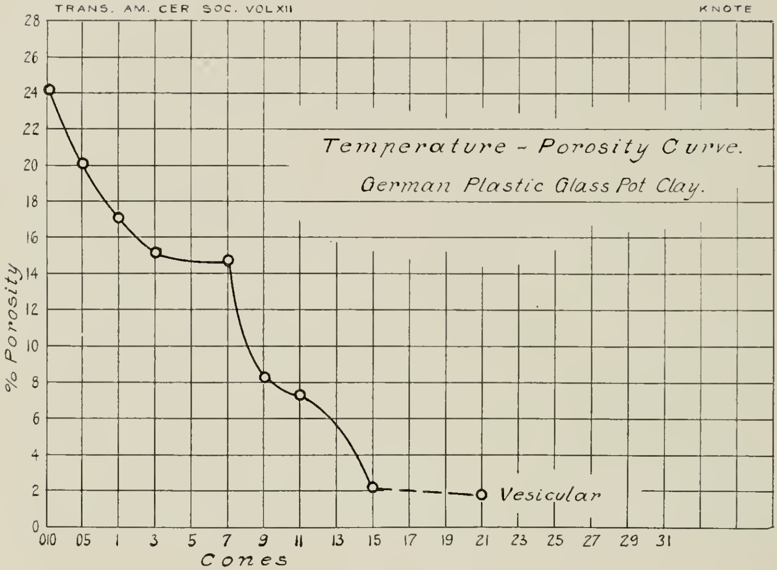
Imported clays are used more or less in the manufacture of glass pots, and as the clay here described is used for this purpose its behavior is of some interest.

Data Obtained on Burned Briquettes.

No.	Heat Treatment Expressed in Cones	Per Cent Fire Shrinkage	Apparent Specific Gravity	Per Cent Porosity
1	010	2.3	2.62	24.4
2	05	2.4	2.62	20.3
3	1	4.3	2.61	17.3
4	3	4.3	2.60	15.8
5	5	...	....	....
6	7	4.6	2.57	15.0
7	9	4.6	2.54	7.7
8	11	4.6	2.50	7.0
9	15	4.2	2.21	2.0
10	20	Vesicular	....	....
11	..	...	....	....


TRANS. AM. CER. SOC. VOL XII.
KNOTE.
Temperatue - Specific Gravity Curve.
German Plastic Glass Pot Clay.
Specific Gravity
2.7
2.6
2.5
2.4
2.3
2.2
2.1
Vesicular
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones


TRANS. AM. CER. SOC. VOL XII
KNOTE.
Temperature - ShrinKage Curve.
German Plastic Glass Pot Clay.
% Fire ShrinKage
14
12
10
8
6
4
2
0
Vesicular
010 05 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31
Cones

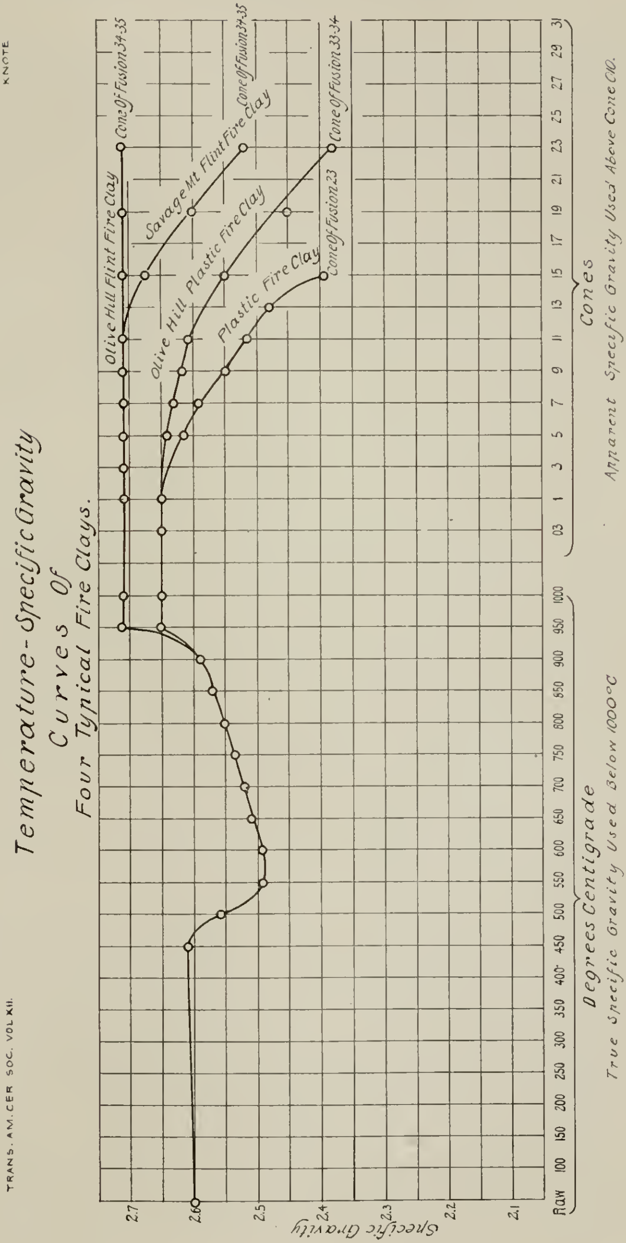


The foregoing curves show that there is a great difference in the behavior of various flint fire clays, and a sharp contrast between the behavior of flint clays and plastic clays.

General Conclusions.

We here present the specific gravity curves of a number of fire clays, all drawn on one sheet. The specific gravity below 1000° C. is true specific gravity, while that above that temperature is apparent specific gravity.

TRANS. AM. CER SOC. VOL XII. KNOTE



For the behavior of clays below 1000° C, we have already advanced an hypothesis, which is formed entirely on experimental data. To explain the behavior above cone 010, we have produced no experimental data, but numerous facts have been brought out by others which help us to formulate an hypothesis.

Numerous writers have pointed out that through sufficiently severe heating all clay wares become more or less crystalline in structure. The clay substance is said to break up into one silicate which is rich in alumina, and another rich in silica. The crystalline substance found in porcelains which have been heated above 1350° C has been identified as sillimanite—(Al_2O_3 SiO_2).

Reasoning from these facts, and our own data, we suggest that on dehydration, kaolinite or clay substance breaks down into two silicates, one rich in alumina and the other rich in silica. These silicates are readily attacked by reagents. At about 950° C a pronounced change takes place, the exact nature of which is still uncertain. If Al_2O_3 2 SiO_2 is formed at this temperature, it becomes unstable as the temperature advances, and is decomposed by the action of fluxes, with the formation of a basic and an acid silicate. If no combination of silicates takes place at 950° C, but the change is due to the formation of isomeric compounds, it is not so easy to explain the phenommena so often pointed out. Experiment alone can decide the question as to what really occurs.

The reactions below cone 010 take place at the same temperatures in the case of both plastic and non-plastic clays, since no constituents are involved other than the clay substance itself. But above that temperature, where other constituents act on the clay substance, there is a striking difference, not in what takes place, but in the temperature at which it takes place. Seger showed clearly that this difference in the behavior of the two types of clay is not necessarily due to difference in chemical composition, but in clays of similar composition to a difference

in physical structure. We may assume then that the difference in the behavior of the plastic and non-plastic clays shown above is primarily due to this cause.

In conclusion, the writer wishes to acknowledge his indebtedness to Mr. B. S. Radcliffe and Mr. A. E. Williams for valuable assistance in securing the foregoing data, and to Professor C. W. Rolfe for granting the use of funds and apparatus which made the work possible.